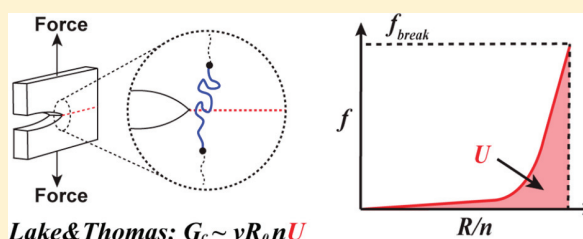


## Quantitative Adjustment to the Molecular Energy Parameter in the Lake–Thomas Theory of Polymer Fracture Energy

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## Supporting Information

**ABSTRACT:** We present a conceptual framework for adding molecular details of chain extension and force-coupled bond dissociation to the Lake–Thomas model of tear energy in rubbery crack propagation. Incorporating data reported from single-molecule force spectroscopy experiments provides an estimate for the stored energy per bond at fracture of  $\sim 60$  kJ mol<sup>−1</sup> for typical hydrocarbon polymers, well below the typical carbon–carbon bond dissociation energy in these systems. Opportunities to test and exploit the role of molecular extension and covalent bond scission in experimental systems are proposed.

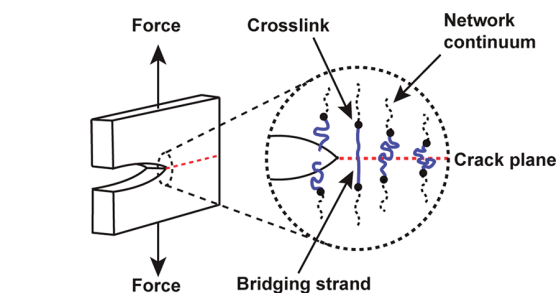
Lake&Thomas:  $G_c \sim \nu R_0 n U$ 

## INTRODUCTION

The fracture of covalent polymer networks limits many of their potential applications, and a quantitative understanding of the molecular mechanisms underlying the mechanical fracture of polymer gels and elastomers might inform methods by which to design more robust polymeric materials. Fracture of a covalent network is inherently molecular, as it requires the scission of covalent chemical bonds. Lake and Thomas<sup>1</sup> recognized over 50 years ago that as a crack propagates across the failing interface of a stretched material, the bonds that fracture across the crack plane are not the only bonds that have stored energy. Rather, the entire chain that initially bridged the crack plane is fully extended. Therefore, the fracture energy must reflect the energy that goes into entropically stretching and enthalpically deforming each repeat unit along this extended chain (and that is lost upon chain scission), so that more energy is put into the system than is required for a single bond scission (Figure 1). The term “bridging strand” here refers to the cross-link-to-cross-link portion of the polymer strand that spans the plane of crack propagation. Lake and Thomas<sup>1</sup> proposed that the fracture energy  $G_c$  is equal to the number of such chains per cross-sectional area ( $\sigma$ ) multiplied by the energy that is required to break one bridging strand ( $W$ ):

$$G_c = \sigma W = \frac{1}{2} \nu R_0 n U \quad (1)$$

where  $R_0$  is the average end-to-end distance of an elastically active network strand (subchain) in its undeformed state,  $\nu$  is the number density of such elastically active subchains,  $n$  is the average number of repeat units along the bridging strand, and  $U$  is the energy that is stored in each repeat unit when the bridging strand breaks. Geometrical arguments give  $\sigma = 1/2 \nu R_0$



**Figure 1.** Schematic illustration of crack propagation at the crack frontier (crack tip). In the dashed circle, the black dots, blue plain strands, and red dashed line represent the cross-links, bridging strands, and crack propagation plane, respectively. Black dashed strands represent the network continuum to which the bridging strands are connected.

as an estimate of the number of elastically active chains per cross-sectional area, where the prefactor of  $1/2$  comes from the projection of the end-to-end vectors of subchains onto the normal of the crack plane.<sup>1</sup> Lake and Thomas argued that  $W$  is proportional to the number of repeat units to give  $W = nU$ . It is worthwhile to note that the fracture energy  $G_c$  in the Lake–Thomas theory does not consider the dissipation (e.g., viscoelasticity or poroelasticity) of real polymeric materials. Our adjustment focuses on the molecular energy parameter in Lake–Thomas theory; hence, dissipation is not considered in the following treatment as well.

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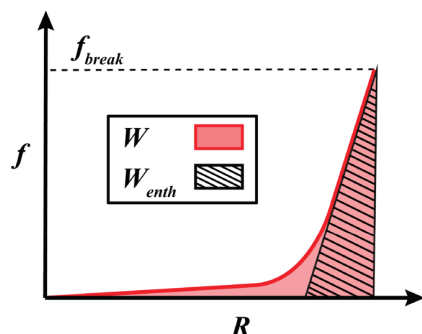
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Here we consider the molecular term  $U$  and its dependence on chemical structure. Equation 1 requires an estimate of  $U$  to have a quantitative predictive value of  $G_c$ . While acknowledging uncertainty in the proper value, Lake and Thomas<sup>1</sup> proposed a seemingly reasonable approximation that the mechanical energy stored in each bond at the time of bridging strand scission might be roughly equivalent to the bond dissociation energy ( $U_{\text{BDE}}$ ) of the weakest bond along the backbone. They also proposed an alternative estimate based on the likely peak force sustained by a Morse potential, i.e., the chemical potential energy  $V(x)$  at the maximum force  $f = dV(x)/dx$  along the Morse potential, where  $x$  is the length coupled to the force. This gives  $U \approx 1/4 U_{\text{BDE}}$  per bond. A survey of the papers that have cited the original Lake–Thomas paper reveals that subsequent attempts to apply the Lake–Thomas theory quantitatively to experimental data have almost exclusively estimated  $U$  in the former manner. For example, Cui used  $U = U_{\text{BDE}}$ <sup>2</sup> and Sakai has similarly taken  $U$  per monomer as the sum of bond energies in a monomer.<sup>3,4</sup> The common use of  $U_{\text{BDE}}$  is a historical (and now unnecessary) artifact, likely stemming from the initial approximation put forth by Lake and Thomas and its ease of implementation. As we show below, it is also incorrect and, as suggested by Lake and Thomas at the time, significantly overestimates the true value of  $U$  that is relevant to the physics assumed in the theory.

## ■ APPROACH AND RESULTS

Recall that  $W$  is the energy that goes into the polymer chain when the chain is overextended to the point that it breaks. In other words, it is the area under the force–extension curve of a representative elastically active strand in the polymer network that is stretched until it breaks<sup>5</sup> (the light red shaded region  $W$  in Figure 2). Therefore, the energy  $U$  (per bond, per



**Figure 2.** Work done to extend a polymer chain is the area (light red shaded region  $W$ ) under the force vs end-to-end distance curve (red curve) up to the force at which the chain breaks ( $f_{\text{break}}$ ) denoted by the dashed horizontal line), at which point all of the energy  $W$  is dissipated. One can divide  $W$  by  $n$  to obtain  $U$ , which is the energy stored in the repeat unit (per bond, per monomer, etc.). The enthalpic part of the energy stored in all repeat units is the area shaded by black lines, which is denoted by  $W_{\text{enth}}$ . Figure is schematic only, and certain features are exaggerated for visual clarity over numerical accuracy.

monomer, per Kuhn segment, etc.) could be obtained by dividing  $W$  by the number of repeat units ( $U = W/n$ ). Unlike 50 years ago, computation and single-molecule force spectroscopy (SMFS) allow for a direct measure of  $W$  and thus of  $U$  that conforms exactly to the physics of the Lake–Thomas

theory, but we are unaware of fracture theories that incorporate this knowledge.

This approach to  $W$  is general, but the precise form of the force–extension curve (Figure 2) depends on the composition of the polymer. It is useful to examine a specific example, and here we consider the case of a polymer whose behavior is captured by the modified freely jointed chain (m-FJC) model (eq 2),<sup>6,7</sup> which accounts for both the low-force, entropy-dominated (square brackets in eq 2) and high-force, enthalpy-dominated extension (parentheses in eq 2) of many synthetic polymers:

$$R = L_0 \left[ \coth \left( \frac{f}{f_c} \right) - \frac{f_c}{f} \right] \left( 1 + \frac{f}{f_s} \right) \quad (2)$$

where  $R$  is the average of end-to-end distance,  $f_c$  is the characteristic conformational tension, and  $f_s$  is the characteristic stretching tension. The characteristic conformational tension  $f_c$  describes the force at which the chain size  $R$  approaches unstretched contour length  $L_0$ . Linear response of chain size for  $f \ll f_c$  implies that  $f_c = kT/b$ , where  $b$  is Kuhn length,  $k$  is Boltzmann's constant, and  $T$  is the absolute temperature. The characteristic stretching tension  $f_s$  describes the linear enthalpic extension of contour length  $L = L_0(1 + f/f_s)$  at  $f \ll f_s$ . Note that the polymer chain breaks at  $f_{\text{break}}$ , which is less than  $f_s$ . The single molecule extensions of typical synthetic polymers are fit with m-FJC with two characteristic tensions separated by 3 orders of magnitude. The characteristic conformational tension of  $f_c \approx 7$  pN if expressed as  $kT/b$  leads to Kuhn length<sup>8</sup>  $b = 0.6$  nm, which is approximately half the value expected from chain size and linear response for  $f \ll f_c$ . The characteristic stretching tension of  $f_s \approx 12$  nN is usually written as  $f_s = k_{\text{seg}} b$ , where the Kuhn segment stiffness<sup>8</sup>  $k_{\text{seg}} = 20$  nN nm<sup>-1</sup>. Below we use these typical values of characteristic tensions. As established by work in polymer mechanochemistry, the probability of bond scission under tension is determined not by the energy of distortion, but by the force applied to the polymer strand.<sup>9,10</sup> Therefore, integrating the m-FJC force–distance curve up to a typical breaking force of  $f_{\text{break}} \approx 4.5$  nN<sup>11,12</sup> gives a value of  $W \approx 18.5$  nN·nm for a typical chain with an unperturbed contour length  $L_0 = 21$  nm consisting of  $n = 175$  main chain bonds (calculation shown in the Supporting Information). Recall that  $W = nU$ , and the terms  $n$  and  $U$  in eq 1 can be defined as the number of, and the energy per each, representative repeat units along the polymer backbone (per bond, per chemical repeat unit, etc.). It might seem that the Kuhn segment is the most convenient repeat unit for m-FJC. However, the typical Kuhn length obtained by fitting the experimental force–extension data to the m-FJC chain model ( $b = 0.6$  nm) is usually smaller than the values  $b \approx 1.1$  nm obtained from measurements of the unperturbed chain size.<sup>8,13</sup> Here, we consider the energy  $U$  as the average elastic energy stored per bond when the polymer chain breaks, and  $n$  is the average number of backbone bonds per bridging strand. Therefore, if the Kuhn segment ( $b = 0.6$  nm) contains approximately five main chain C–C bonds, the m-FJC model gives the length per bond  $l = 0.12$  nm along the stretching coordinate and a stored elastic energy per bond of  $U \approx 64$  kJ mol<sup>-1</sup> when the polymer chain breaks.

The energy  $U$  is dominated by the enthalpic distortion; if the entropic contribution is ignored and only the work going into Hookean stretching of the segments is considered, we denote the enthalpic distortion energy stored in a polymer chain as

$W_{\text{enth}}$  (Figure 2; black lines shaded region), and the enthalpic distortion energy per bond ( $U_{\text{enth}} = W_{\text{enth}}/n$ ) would be given by eq 3

$$U_{\text{enth}} = \frac{1}{2} \frac{f_{\text{break}}^2}{f_s} l \quad (3)$$

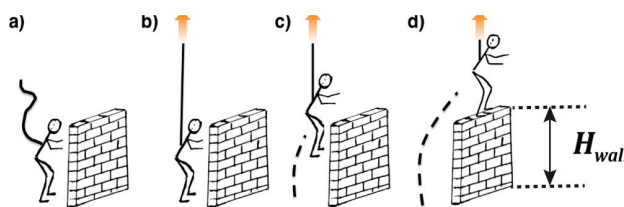
which for the model system with  $l = 0.12$  nm,  $f_s = 12$  nN, and  $f_{\text{break}} = 4.5$  nN gives  $U_{\text{enth}} \approx 61$  kJ mol<sup>−1</sup>. The contribution of conformational entropy to  $U$  in this case, therefore, is only  $\sim 3$  kJ mol<sup>−1</sup>, or about 5% of the total energy ( $U \approx 64$  kJ mol<sup>−1</sup>). Therefore, a convenient approximation of the energy stored in a polymer chain near its breaking condition is given by  $W = nU \approx W_{\text{enth}} = nU_{\text{enth}}$ .

A few points are worth considering. First, the length of chain contour  $L_0$  used in this treatment should take into consideration the network model. In particular, for materials that obey the physics of phantom networks, one should use not just the average length  $L_0$  of the strands between cross-links, but the adjusted length of the combined strand.<sup>13</sup> Second, the linear approximation of the dependence of contour length on the applied force  $L = L_0(1 + f/f_s)$  may not be valid all the way up to the typical forces  $f_{\text{break}}$  of conventional bond scission (4–5 nN), and we do not have an experimental confirmation of where the linear approximation breaks down since experimental force–extension curves rarely if ever reach such high force. Third, the force dependence of the bond lifetime<sup>10,14</sup> is well-known to lead to the actual value of  $f_{\text{break}}$  that is loading rate dependent,<sup>11,15</sup> and so the strain rate and time scale of crack propagation and the force-coupled kinetics of scission should be taken into account in a more rigorous treatment. Finally, recall that  $U$  is the average energy stored *per bond* in previous paragraphs, meaning each bond is storing only  $\sim 60$  kJ mol<sup>−1</sup> at the time of chain scission. This value is well below the  $U_{\text{BDE}}$  of a typical covalent bond along a synthetic polymer backbone ( $\sim 350$ – $370$  kJ mol<sup>−1</sup>)<sup>16</sup> and is in reasonable agreement with the original experimental data considered by Lake and Thomas.

## DISCUSSION

The low value of  $U$  obtained from this analysis might appear to be unrealistic for the same reason cited by Lake and Thomas in motivating their original proposal: namely, it seems intuitively reasonable that the work done on a bond should be comparable to the thermodynamic strength of that bond, or else the bond would remain intact. The (understandable) misconception inherent in this argument is that the mechanical work that assists bond scission is stored in the intact bond. In fact, however, the critical work that is responsible for assisting bond scission is the work that is *coupled to the reaction, not stored in the reactant*. We next explain this important distinction and its implications through an analogy that we subsequently connect back to real polymer systems.

Imagine a conceptual “model reaction” of a person trying to make a standing jump from the floor (reactant, Figure 3a) to land on her or his feet atop a six-foot wall (product, Figure 3d). Reaching the top of the wall is chosen to be analogous to breaking a covalent bond, and the gravitational force between person and floor represents the covalent forces that bind the atoms in the weakest bond along a polymer strand. Undoubtedly, she/he cannot muster enough energy to surmount that barrier. Now consider the case where that same individual is tethered to a bungee cord, and then that

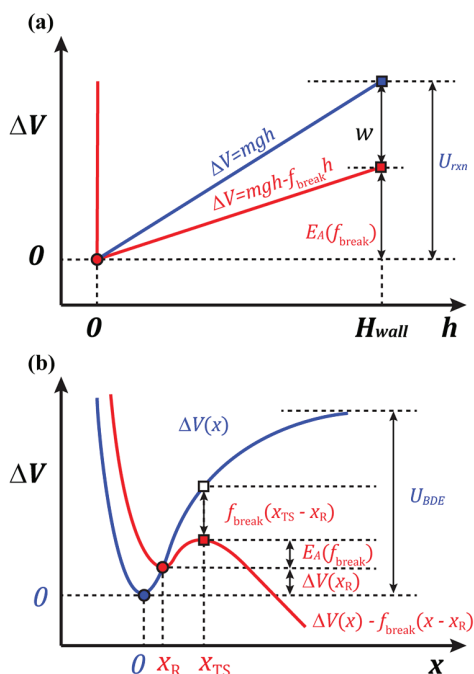


**Figure 3.** (a) A person wearing a slack bungee cord is unable to jump to the top of a tall wall of height  $H_{\text{wall}}$ . (b) The bungee cord is stretched without performing work on the person until (c) the person jumps, at which point potential energy is transferred from bungee cord to the person, allowing the jumper to surmount the wall (d). The physics of this example are analogous to why the energy of distortion put into the average bond in a strained network strand at chain scission can be so much smaller than the energy required to break the bond.

bungee cord is stretched quite tight—but not tight enough to lift on its own the person from the floor (Figure 3b). Now, the same jump that would have failed to reach the top of the wall without the assistance of the bungee cord might easily transport the person to the top of the wall with the bungee cord assistance (Figure 3c,d). The stretched bungee cord, in this case, helps to break the “gravitational bond”, but this is not because the gravitational component of the potential energy has changed before the person leaves the floor (as the person’s center of mass has not moved much while she/he is still standing on the floor even with the bungee cord attached). Rather, the stored elastic energy in the bungee cord is coupled to the jump. In this example, the energy is stored almost entirely in the elastically stretched cord and not in the gravitational energy related to the displacement of the jumper from the floor.

To further understand the “assisted jumper” metaphor, consider the undisturbed and the force-coupled potential difference profiles  $\Delta V$  of this “bond” (Figure 4a, highlighted in blue and red, respectively). When the bungee cord is relaxed (Figure 3a), the “bond” is under zero tension, and it is in its ground state (red dot in Figure 4a). After the bungee cord is stretched (Figure 3b), the force-coupled potential difference  $\Delta V$  of this “bond” is changed (red curve in Figure 4a). The bond length, however, is still at the same ground state value (red dot), which means *no work has yet been performed on this “bond”*, despite the fact that the work was performed on the bungee cord. When the person starts to jump (Figure 3c,d), the “bond energy difference” follows the red potential curve toward the red square (Figure 4a). The energy required to reach the top of the wall is now the force-coupled activation energy  $E_A(f_{\text{break}})$ , as the remainder of the energy  $w = U_{\text{rxn}} - E_A(f_{\text{break}})$  needed to surmount the barrier is supplied from the energy that is stored in the bungee cord. One could use the precise formula for the energy of an extended spring, but for simplicity (and in analogy to many polymer mechanochemical systems), we consider the case in which the extension of the bungee cord is very large relative to  $H_{\text{wall}}$ , so that the jumper experiences an effectively constant force  $f_{\text{break}}$  over the height of the jump, and  $w = f_{\text{break}}H_{\text{wall}}$ . Although  $f_{\text{break}}H_{\text{wall}}$  comes from the work that we put into the bungee cord, the “bond” does not obtain it unless and until the reaction happens. Note that the undisturbed and the force-coupled scenarios have different ground states, since the ground state of the force-coupled situation contains the energy that we put into the bungee cord (which corresponds to  $W$  in eq 1), and this energy is





**Figure 4.** Schematic illustrations of the undisturbed (blue) and the force-coupled (red) profiles of potential for (a) “assisted jumper” metaphor and (b) the tilted potential energy profile (t-PEP) model. Here, the t-PEP is meant to represent the per bond normalized energetic contributions of all distortions (in bond lengths, angle, and torsions) associated with deformation. For (a), the  $\Delta V$  axis and  $h$  axis represent the difference of potential and the distance of the jumper to the floor, respectively.  $H_{\text{wall}}$  represents the height of the wall. The undisturbed potential difference gives  $\Delta V = mgh$ , where  $mg$  is the weight of the jumper.  $U_{\text{rxn}}$  represents the energy that is required to make this “reaction” happen in the undisturbed state. The force-coupled potential difference gives  $\Delta V = mgh - f_{\text{break}}h$ , where  $f_{\text{break}}$  is the tension on the bungee cord pulling the jumper, which is approximately a constant. The activation energy  $E_A(f_{\text{break}})$  is the energy that the jumper needs to overcome, while  $w = f_{\text{break}}H_{\text{wall}}$  is the work performed by the bungee cord during the jump. For (b), the  $\Delta V$  axis and  $x$  axis represent the potential energy difference and the force-coupled length relative to the undeformed reactant, respectively.  $U_{\text{BDE}}$  represents the dissociation energy of bonds along the unstretched polymer. The activation energy  $E_A(f_{\text{break}})$  is the energy that the breaking bond needs to overcome by thermal motion ( $E_A(f_{\text{break}}) < U_{\text{BDE}}$ ), while there is an additional work  $f_{\text{break}}(x_{\text{TS}} - x_{\text{R}})$  (difference between white square and red square) that is coupled to the reaction (analogous to  $w = f_{\text{break}}H_{\text{wall}}$ ). Note that  $x_{\text{TS}}$  and  $x_{\text{R}}$  depend on  $f_{\text{break}}$  since  $f_{\text{break}} = d\Delta V(x_{\text{TS}})/dx_{\text{TS}} = d\Delta V(x_{\text{R}})/dx_{\text{R}}$ . The force-coupled potential difference is  $\Delta V(x) - f_{\text{break}}(x - x_{\text{R}})$ , where  $\Delta V(x)$  is the undisturbed profile of the potential difference. Because the curve is tilted by the applied force, the ground-state coordinate moves from  $x = 0$  (with zero force) to  $x = x_{\text{R}}$  (with force  $f_{\text{break}}$ ). The energy difference between the undisturbed and the force-coupled ground states is  $\Delta V(x_{\text{R}})$ , which corresponds to the energy stored in each bond when the force is applied.

subtracted when we plot  $\Delta V$  vs  $h$ . We emphasize that  $U$  in eq 1 does not correspond to  $f_{\text{break}}H_{\text{wall}}$ ; the work  $f_{\text{break}}H_{\text{wall}}$  is the work coupled to the reaction (the bond scission), while  $W = nU$  in eq 1 corresponds to the energy stored in the bungee cord.

The key point of this model is that the energy stored in the reactant is very different from (and can be much less than) the work that assists the reaction. Returning to the actual scission of a polymer chain, a similar effect is present. Consider a

polymer chain that obeys the tilted potential energy profile (t-PEP) model.<sup>10,15</sup> As shown in Figure 4b, the undisturbed and the force-coupled potential profiles of each bond based on the t-PEP model are highlighted in blue and red, respectively. When the external force is applied to the polymer chain, the coordinate  $x$  corresponding to the minimum energy of each bond moves from the blue dot ( $x = 0$ ) to the red dot ( $x = x_{\text{R}}$ ) by tilting the potential profile. Different from the common t-PEP model, the ground state of the force-coupled potential profile (red curve in Figure 4b) crosses the undisturbed potential profile at  $x = x_{\text{R}}$ , which is the point at which the external force is equal in magnitude to  $d\Delta V/dx$ , the derivative of the chemical potential ( $f_{\text{break}} = d\Delta V(x_{\text{R}})/dx_{\text{R}}$ ). The energy difference between the blue dot and the red dot indicates that each bond is distorted, but with the elastic energy stored in each bond  $\Delta V(x_{\text{R}})$  that is lower than  $U_{\text{BDE}}$ . Note that this is the energy that is stored in the reactant and that it corresponds to the per bond contribution to the Lake–Thomas energy  $U = \Delta V(x_{\text{R}})$  in eq 1. As a given bond starts to break, it overcomes  $E_A(f_{\text{break}})$  by thermal motion (moving from the red dot to the red square in Figure 4b), while there is additional work  $f_{\text{break}}(x_{\text{TS}} - x_{\text{R}})$  that is coupled to the reaction of this bond, which is analogous to the work  $w = f_{\text{break}}H_{\text{wall}}$  in Figure 4a. On the other hand, the ground state of the other bonds will move back from (on average) the red dot toward the blue dot, thereby releasing the stored elastic energy  $U = \Delta V(x_{\text{R}})$  per bond as heat. Hence, the energy required to facilitate the breakage of a polymer chain is recovered from the potential energy that has been put into each bond along the strand at the time that the polymer breaks; the springlike distortions of the segments mimic the extension of the bungee cord in Figure 3. Dividing the energy  $W$  that is stored in a whole chain when the chain breaks by the number  $n$  of bonds gives  $U$  in eq 1, as when the chain breaks all coupled bonds relax fully from the red dot to the blue dot, and the stored energy  $\Delta V(x_{\text{R}})$  per bond is released.

While the treatment presented here assumes that the enthalpic distortion of the polymer is Hookean ( $f_{\text{break}}$  is constant), some deviation from the ideal Hookean behavior is expected.<sup>17,18</sup> Nonetheless, prior computational work suggests that the nonlinear behavior within the enthalpic distortion regime should make a minor contribution to  $U_{\text{enth}}$ ; the error introduced is likely to be very small relative to the use of  $U_{\text{BDE}}$  and comparable to that introduced by the uncertainty in the precise value of  $f_{\text{break}}$ . For example, the computational work by Saitta and Klein<sup>19</sup> on linear alkanes predicts the distortion energy per C–C bond repeat of 68 kJ mol<sup>−1</sup>, a difference of <15% of the estimate presented here on the basis of a typical m-FJC behavior.

To summarize, there are two important energies that we would like to differentiate: First, the bond dissociation energy  $U_{\text{BDE}}$  of the undisturbed state, which has been widely used as the energy  $U$  in eq 1,<sup>2–4</sup> is obviously not the energy stored in each bond when the polymer chain breaks. Second, the energy  $\Delta V(x_{\text{R}})$  in Figure 4b is the energy that corresponds to  $U$  in eq 1. When a polymer chain is under tension, each bond stores elastic energy  $\Delta V(x_{\text{R}})$ . As one bond breaks, it is activated by thermal motion and overcomes the barrier  $E_A(f_{\text{break}})$ . Once this bond is broken, other bonds of this chain relax, and each bond releases the stored energy  $\Delta V(x_{\text{R}})$ .

## CONCLUSIONS

A sounder foundation for more accurate estimates of  $U$  should enable more rigorous tests and (if necessary) refinements of

Lake–Thomas and related molecular theories of macroscopic fracture. For example, recent advances in covalent polymer mechanochemistry provide an opportunity to quantify and systematically vary both the breaking force  $f_{\text{break}}$ <sup>20,21</sup> and the shape of the force–extension curve. The molecular designs that empower those studies should consider that (i) the enthalpic contribution to  $U$  is proportional to  $f_{\text{break}}^2$  rather than  $f_{\text{break}}$  (see eq 3; e.g., changing  $f_{\text{break}}$  from 4.5 to 5 nN results in a 23% increase in  $U$  from 61 to 75 kJ mol<sup>−1</sup>) and (ii) the relationship between  $U_{\text{BDE}}$  and  $f_{\text{break}}$  is not simple; sometimes higher  $U_{\text{BDE}}$  is associated with lower  $f_{\text{break}}$  and vice versa.<sup>21</sup> One can also imagine changing  $f_s$ , as more compliant bonds (lower  $f_s$ ) will store more energy (see eq 3), just as the elastic bungee cord extension stores more energy than the stiff jumper in our macroscopic metaphor. A more intriguing idea (for quantitative tests as well as potential applications), however, is to increase  $U$  dramatically by fundamentally changing the shape of the force–extension curve, for example, through the incorporation of mechanophores that release large covalent stored length at high force.<sup>22–24</sup> Regardless of the mechanism, ever-improving estimates of  $U$  can now be reliably obtained for both the shape of the force–extension curve and  $f_{\text{break}}$  either experimentally or computationally.<sup>24</sup> When available, direct measurements on the systems of interest are of course preferable. We propose that continued advancements in strand extensional behavior, combined with techniques to control and characterize polymer network topology<sup>25,26</sup> and its effect on the distribution of tension, can lead to fully quantitative and predictive models of polymer network fracture toughness with no adjustable parameters.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b02341.

Calculations related to the modified freely jointed chain (m-FJC) (PDF)

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### Notes

The authors declare no competing financial interest.

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